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ORIGINAL ARTICLE

Dependency of built-in potential of LaF_3/porous-silicon heterostructure prepared by chemical bath deposition technique on the concentration of $LaCl_3$ and annealing temperature

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Abstract Effect of $LaCl_3$ concentration and annealing temperature on the built-in potential of LaF_3/PS heterojunction has been investigated in this report. LaF_3 layers have been deposited by a novel chemical bath deposition (CBD) technique. With this simple technique LaF_3 produced as $LaCl_3$ are made to react with hydrofluoric acid on the porous silicon (PS) substrate. This enables direct deposition of LaF_3 on the pore walls of the PS leading to a successful passivation of PS. The compositions of the deposited LaF_3 were confirmed by energy dispersive of X-ray analysis. The built-in potential decreases with $LaCl_3$ concentration and increases with annealing temperature. Therefore, by changing the $LaCl_3$ concentration and annealing temperature quality of the LaF_3 layer on PS can be optimized. From the experimental results it can be concluded that lanthanum fluorides can be deposited on the PS surface by the CBD technique, which provides the required passivation for PS. This passivation can enable the PS to be considered as an important material for photonics.

Keywords Porous silicon · Passivation · Photonics · Chemical bath deposition (CBD) · Built-in potential

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Introduction

Recently, there has been increasing interest in semiconductor materials, which find applications in optoelectronic, photovoltaic industries and photoelectrochemical solar cell devices. Among these materials, LaF_3 thin films appear to be promising candidates for many technological applications due to their stability, band gap energy (about 10.3 eV) (Pilvi et al. 2008) transparency and photoconductor behavior. A disadvantage of this material is the aging, that is, the slow spontaneous oxidation of porous silicon (PS) (Boukherroub et al. 2000). PS can be considered as a silicon (Si) crystal having a network of voids in it (Andrea Edit Pap, Faculty of Technology, University of oulu, P.O. Box 4000, FIN-90014 University of oulu Finland, http://herkules.oulu.fi/isbn9514277759/). This chemical conversation is slow and basically similar to the aging of Si wafer, i.e., a native oxide layer forms on the surface of the pores and the thickness of this oxide layer grows with time. Due to the aging effect, the structural, compositional, electrical and optical properties of PS show continuous change with storage time (Boukherroub et al. 2000). That is many of its properties, such as photoluminescence, are age-dependent and unstable. Tischier et al. observed that the exposure of PS in different ambient results in a rather rapid decrement of photoluminescence (PL) intensity (Fan 2014). One possible way to reduce the aging effect could be "passivation" of PS. Passivation is defined as the process of forming a protective film on an active material surface to reduce the chemical reactivity of the surface and protect it against contamination and increase its stability by isolating the surface from chemical and electrical conditions in the environment. Over the years, many passivation methods, such as anodic oxidation and rapid thermal oxidation, have been attempted to

improve the stability, as well as efficiency, of PS. However, these passivation methods always carry the danger of a total oxidation of the PS layer and of transforming it into SiO_2. Because of various advantages of LaF_3 like good moisture resistance (Hopkins et al. 1975), large bad gap (Pilvi et al. 2008), passivation of PS has been investigated for the first time in our previous articles (Mortuza et al. 2012). By reacting $LaCl_3$ with hydrofluoric acid (HF), LaF_3 has been tried to deposit into the pores of PS surface with a goal of not to allow the PS sample to be oxidized during transportation and drying for passivation like other deposition techniques (Mortuza et al. 2012). This article reports the influence of $LaCl_3$ concentration and annealing temperature on the built-in potential of LaF_3/PS structure. The potential where $1/C^2$–V curve intersects with x-axis is the built-in potential.

Experimental

The PS has been prepared in the home-made double tank cell by anodic etching of silicon wafer (Halimaoui 1997) (Fig. 1). The anodic etching of Si was done in a 1:1 (for n-type silicon) solution of 48 % HF and absolute ethanol and for p-type it was 3:1. The LaF_3 films with different $LaCl_3$ concentration and annealing temperatures were prepared.

Just after the anodic etching the etching solution was drained out and the fresh HF was introduced in the chamber to wash out any remaining etching solution on the chamber. After draining out the washing HF, solution of $LaCl_3$ and 48 % HF were introduced simultaneously into the etching chamber to initiate the chemical reaction and produces LaF_3 that deposits on the just prepared PS sample. Thus, the PS is never exposed to the environment before passivation and this CBD method of LaF_3 deposition should prevent the PS to be oxidized. The $1/C^2$–V (where C represents capacitance and V represents voltage) plots of different samples are drawn and from where the built-in potentials are calculated. The built-in potential decreases with $LaCl_3$ concentration and increases with annealing temperature.

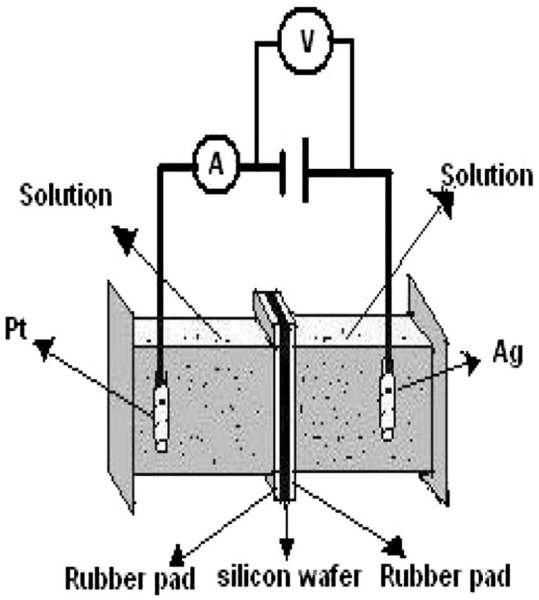

Fig. 1 Schematic drawing of a double-tank chamber for PS fabrication

Anodic etching was carried out using an electrolyte of HF (48 %) and ethanol (98 %) in 1:1 proportion under a constant current density of 15 mA/cm^2 for 30 min at room temperature. The electrochemical anodization of Si wafer was done using a double tank cell set-up (Mortuza et al. 2012). The wafer was cut into pieces and these pieces of Si wafer were cleaned by successively immersing in acetone, ethanol and deionized water. The electrolyte consisted of HF:C_2H_5OH in the ratio of 3:1 by volume(for p-type Si wafer). A 100 W tungsten lamp was used for illumination from 15 cm distance. After 30-min anodization, the etching solution and back contact solution was drained out keeping the samples in the etching chamber (Halimaoui 1997). Fresh HF was then introduced in the chamber to wash out any remaining etching solution on the chamber. After draining out the HF that used for washing, 0.2, 0.4 or 0.6 solution of $LaCl_3$ and 48 % HF were introduced simultaneously into the etching chamber through the "HF in" and "$LaCl_3$ in" channels to do the chemical reaction. The chemical reaction that produces LaF_3 is pretty simple, at room temperature, the addition of hydrofluoric acid to an aqueous solution of lanthanum chloride precipitates out lanthanum fluoride, LaF_3 (Patnaik 2002). The formation of white precipitate (LaF_3) confirmed the mechanism of film formation. The basic reaction during LaF_3 deposition is given below:

$$LaCl_3 + 3HF \rightarrow LaF_3 + 3HCl$$

The solution inside the etching chamber was stirred for 10 s and resulting LaF_3 crystals were allowed to passivate the PS layer for 4 min. After each cycle of reaction, the solution was drained out through the "Solution out" channel and a new solution was introduced into the chamber for the next deposition cycle. In this case, the deposition results from a chemical reaction in solution, which may involve the surface silicon atoms, and in this case, we will speak of chemical grafting of the surface, and why the reaction is limited to the formation of one monolayer (Herino 2000). The whole process was repeated to obtain the various thickness of LaF_3 on to PS. After completing the required cycle the wafer was removed from the chamber, rinsed with de-ionized water and dried in air at room temperature.

The compositional investigations have been done by the energy dispersive X-ray (EDX) spectroscopy. For Capacitance–Voltage (C–V) characterization of the lanthanum fluoride deposited PS sample, silver (Ag) film was evaporated onto the front and backside of the sample in a small area using Edwards E-306A vacuum coating unit. Then the C–V study was done by an impedance analyzer (HP 4294A). The C–V measurement was done in room temperature and in a dark chamber at 500 Hz. From this C–V study the $1/C^2$–V plots of different samples are drawn.

Results and discussion

The chemical-bath deposited LaF_3 on PS produces a heterostructure system (LaF_3/PS/Si). The $1/C^2$–V curves for different samples from which we can determine built-in potential are shown in Figs. 2, 3 and 4 and the built-in potentials for those samples are listed in Table 1.

From Table 1 it is clear that the built-in potential for different samples is different. The variations of built-in potential with $LaCl_3$ concentration and annealing temperature are shown in Figs. 5 and 6, respectively.

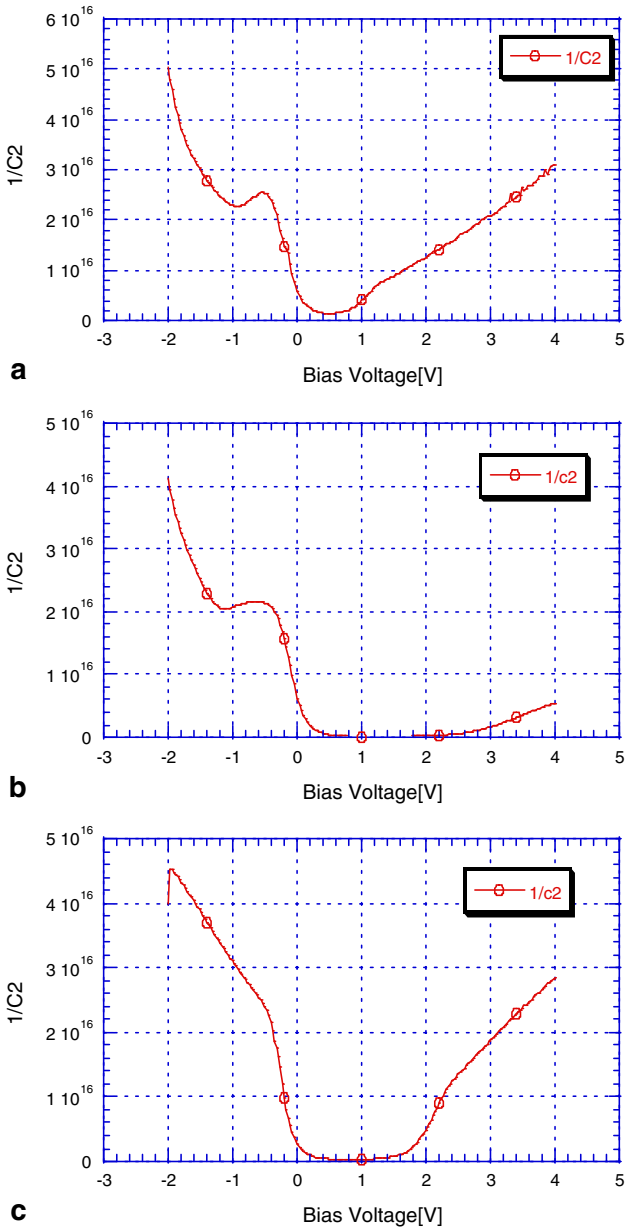

Fig. 2 $1/C^2$–V plots of: **a** 0.2 M (sample#1), **b** 0.4 M (sample#2) and **c** 0.6 M (sample#3) samples at 200° annealing temperature

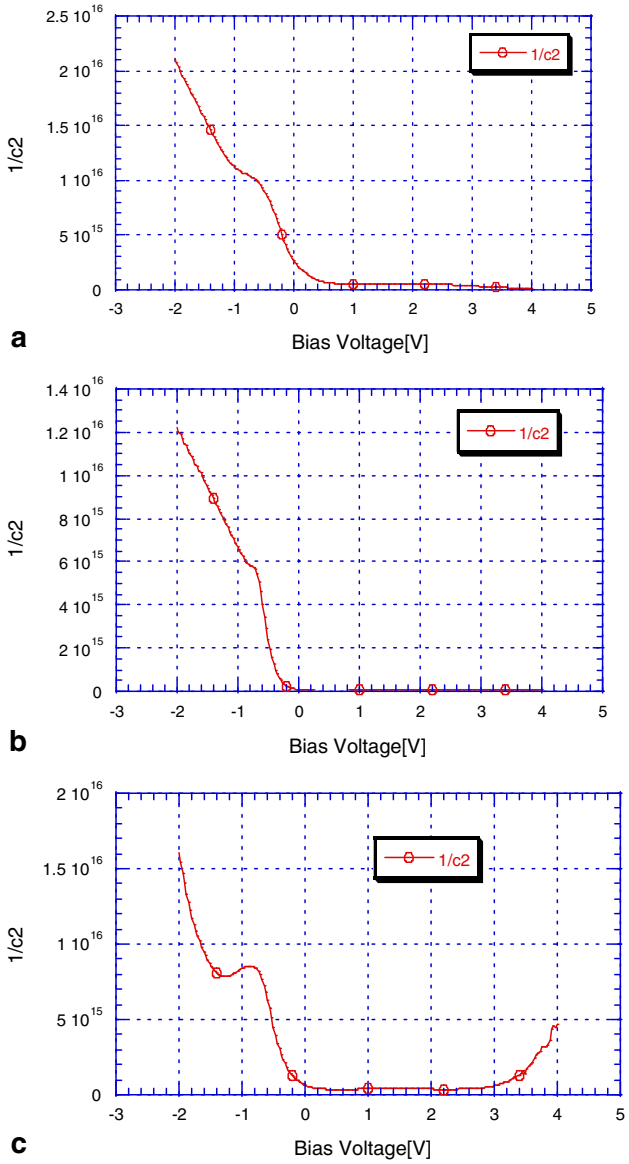

Fig. 3 $1/C^2$–V plots of: **a** 0.2 M (sample#4), **b** 0.4 M (sample#5) and **c** 0.6 M (sample#6) samples at 600° annealing temperature

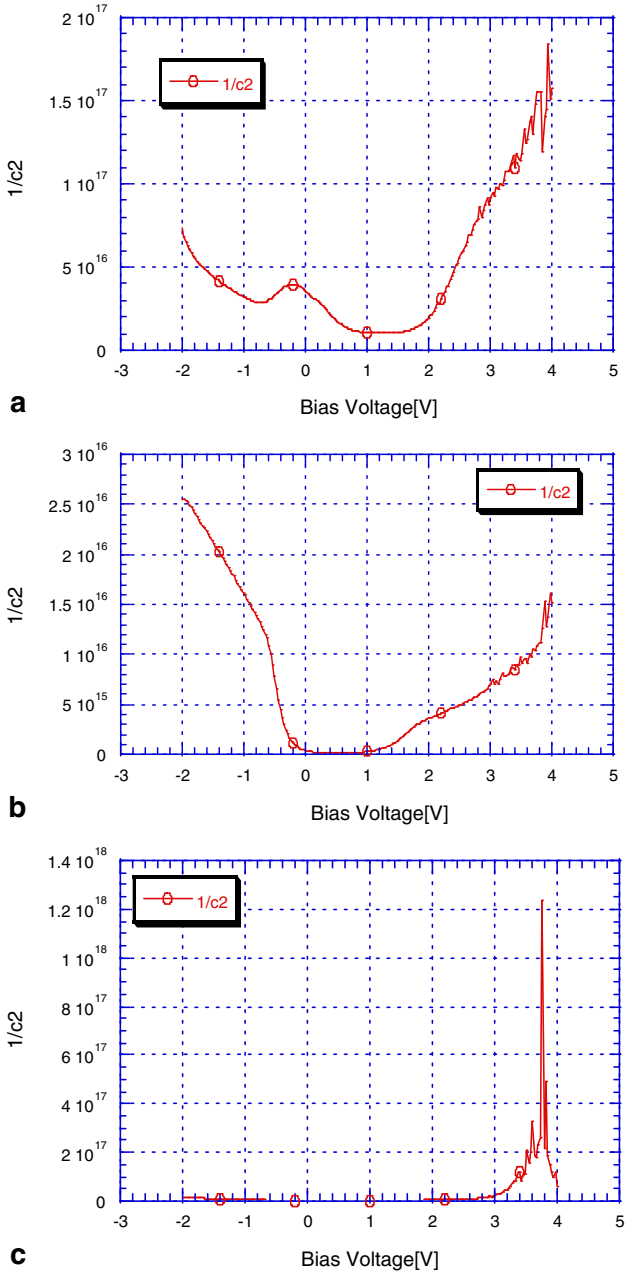

Fig. 4 $1/C^2$–V plots of: **a** 0.2 M (sample#7), **b** 0.4 M (sample#8) and **c** 0.6 M (sample#9) samples at 400° annealing temperature

Table 1 List of built-in potential for different samples at 500 Hz

Sample no.	Built-in potential (*V*)
1	0.5
2	1
3	1
4	4
5	3.5
6	2.2
7	1
8	1
9	2.2

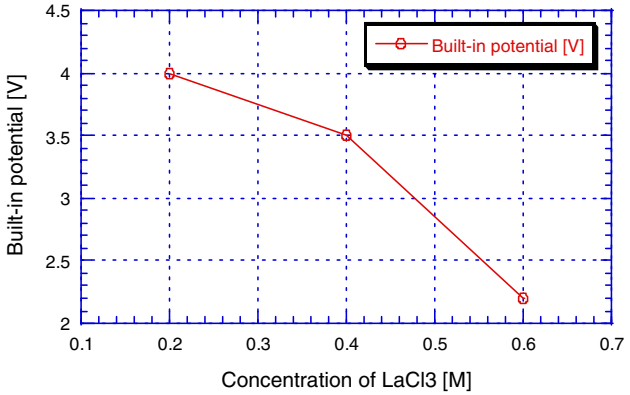

Fig. 5 Variation of built-in potentials with $LaCl_3$ concentration for 600 °C annealed samples

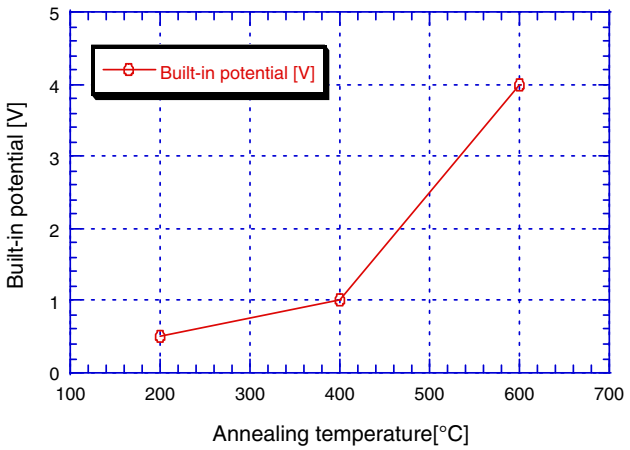

Fig. 6 Variation of built-in potentials with annealing temperature for 0.2 M $LaCl_3$ samples

From Figs. 5 and 6 it is clear that the built-in potential decreases with $LaCl_3$ concentration and increases with annealing temperature.

In this report LaF_3 was deposited on PS by CBD technique with a home-made double tank cell setup. From the EDX data, it was confirmed that the LaF_3 was deposited on PS in the in situ technique. Later, the influence of $LaCl_3$ concentration and annealing temperature on the built-in potential of LaF_3/PS structure has been investigated. The built-in potential decreases with $LaCl_3$ concentration and increases with annealing temperature. It might be due to the reduction and increment of LaF_3 layer thickness.

Conclusions

Hence, from this research, it can be concluded that LaF_3 can be efficiently deposited on PS by the CBD technique. The aim of the thesis was to investigate the influence of $LaCl_3$ concentration and annealing temperature on the built-in potential of LaF_3/PS structure. The EDX confirmed the deposition of LaF_3 on PS.

From these experimental results it can also be concluded that the passivating layer of LaF_3 on PS can be optimized by the $LaCl_3$ concentration and annealing temperature. This optimized layer of LaF_3 can enable the PS to be an important material in electronic and optoelectronic device fabrication.

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